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SYNTHESIS OF NEW GEM-DIALKYLTETRACHLOROPHOSPHAZENES VIA 'METALL--ETC(U)
APR 79 P J HARRIS, H R ALLCOCK N00014-75-C-0685
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The reaction of hexachlorocyclotriphosphazene with organocopper reagents leads to the synthesis of a highly reactive phosphazene-copper intermediate. This intermediate reacts with alkyl halides to yield a range of hitherto inaccessible alkylphosphazenes, including several with unsaturated alkyl side groups. These cyclic oligomer reactions are model systems for the analogous high polymers.

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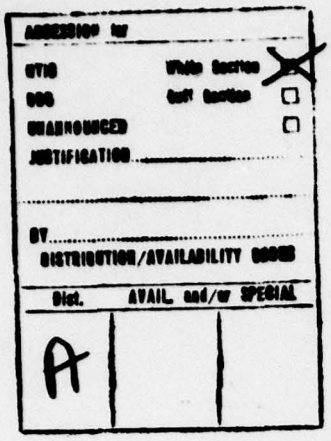

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Technical Report No. 8

SYNTHESIS OF NEW GEM-DIALKYLTETRACHLOROPHOSPHAZENES VIA "METALLOPHOSPHAZENE" INTERMEDIATES

by

Paul J. Harris and Harry R. Allcock*

Prepared for publication in the Journal
of the Chemical Society, Chemical Communications

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April 26, 1979

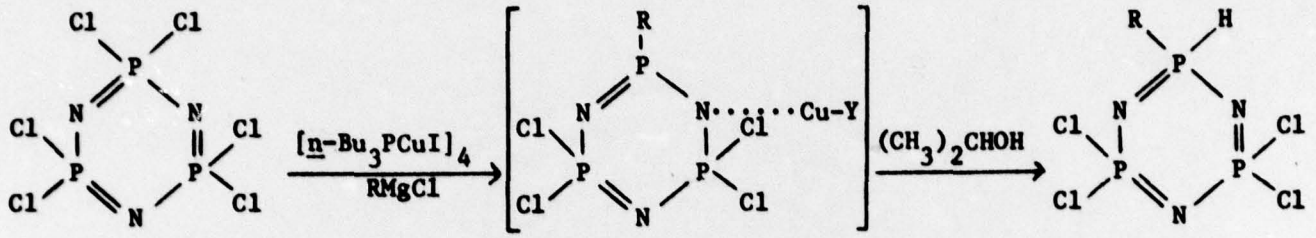
Synthesis of New Gem-Dialkyltetrachlorophosphazenes via "Metallophosphazene" Intermediates

by Paul J. Harris and Harry R. Allcock*

(Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802)

Summary. A new method has been found for the synthesis of alkylcyclophosphazenes. The reaction pathway utilises a highly reactive copper -phosphazene intermediate (II) prepared by the reaction of $(NPCl_2)_3$ with a Grignard reagent and $[n\text{-}Bu_3PCuI]_4$. The reactions of alkyl halides with II yield a wide variety of gem-dialkyltetrachlorocyclotriphosphazenes. 1-Bromo-2-butene or propargyl bromide react with II to yield the 3- substituted 1,2- butenyl and propadienyl derivatives, respectively.

In an earlier communication[1] we described the synthesis of hydridocyclophosphazenes, $N_3P_3Cl_4HR$ (III) by the interaction of $(NPCl_2)_3$ (I) with alkylmagnesium halides in the presence of $[\underline{n}\text{-}Bu_3PCuI]_4$. This reaction was presumed to proceed through the formation of a metallophosphazene intermediate (II).



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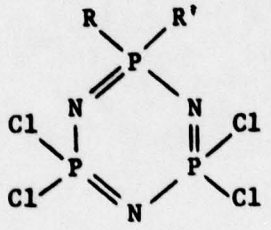

IV

Species II has not yet been isolated. However, we have now demonstrated the broad utility of II as a synthetic intermediate by the preparation in high yield of a range of hitherto inaccessible gem-dialkylcyclotriphosphazenes of structure IV. This reaction route constitutes a powerful addition to the available methods[2-5] for the attachment of organic residues to a phosphazene skeleton through carbon-phosphorus bonds.

The specific reaction conditions for the formation of IV are as follows. Hexachlorocyclotriphosphazene (I) (5.0 g, 14.37 mmol) and $[\underline{n}\text{-}Bu_3PCuI]_4$ (4.0 g,

2.53 mmol) were stirred in tetrahydrofuran (150 ml) at -80°C, and the Grignard reagent (56 mmol) was then added dropwise. The reaction mixture was allowed to warm slowly to 25°C and was then stirred for 14 hr to optimize the yield of II. The mixture was then cooled to 0°C, the alkyl halide (42 mmol) was added, and stirring was continued at 25°C for a further 20 hr. The product (IV) was isolated in more than 70% yield (based on the amount of I) after recrystallization from n-hexane. All the species of structure IV were characterized by infrared and ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy, mass spectrometry, and elemental analyses.

The versatility of this synthesis route is illustrated by the data shown in the Table. Of particular interest is the observation that 1-bromo-2-butene and propargyl bromide react with II by a 1,4- addition route. This behavior is typical of many organo-copper reagents.[6] Thus, although the structure of II has not yet been determined unambiguously, its reactivity patterns are compatible with an "organo-copper"-type intermediate, as suggested in the structure shown.

Acknowledgement. We thank the U.S. Office of Naval Research for the support of this work.

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Table

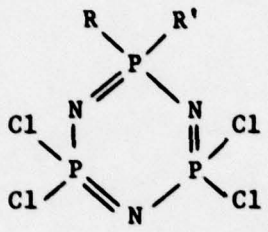
Products of Formula $N_3P_3Cl_4RR'$ (IV Formed from Copper-Phosphazene Intermediates

Grignard Reagent RMgCl	Organic Halide R'X	Phosphazene Substituents R	R' or R" [a]
CH_3MgCl	CH_3I	$-CH_3$	$-CH_3$
CH_3MgCl	$CH_2=CH-CH_2Br$	$-CH_3$	$-CH_2-CH=CH_2$
CH_3MgCl	$CH_3-CH=CH-CH_2Br$	$-CH_3$	$-CH(CH_3)-CH=CH_2$
CH_3MgCl	$CH\equiv C-CH_2Br$	$-CH_3$	$-CH=C=CH_2$
CH_3CH_2MgCl	CH_3I	$-CH_2CH_3$	$-CH_3$
$CH_3(CH_2)_2MgCl$	CH_3I	$-(CH_2)_2CH_3$	$-CH_3$
$CH_3(CH_2)_3MgCl$	CH_3I	$-(CH_2)_3CH_3$	$-CH_3$
$(CH_3)_2CHMgCl$	CH_3I	$-CH(CH_3)_2$	$-CH_3$
$(CH_3)_2CHMgCl$	$CH_2=CH-CH_2Br$	$-CH(CH_3)_2$	$-CH_2-CH=CH_2$
$(CH_3)_3CMgCl$	CH_3I	$-C(CH_3)_3$	$-CH_3$
$(CH_3)_3CMgCl$	$CH_2=CH-CH_2Br$	$-C(CH_3)_3$	$-CH_2-CH=CH_2$
$CH_2=CH-CH_2MgCl$	CH_3I	$-CH_2-CH=CH_2$	$-CH_3$
$CH_2=CH-CH_2MgCl$	$CH_2=CH-CH_2Br$	$-CH_2-CH=CH_2$	$-CH_2-CH=CH_2$

[a] R" represents a rearranged side group

Justification

In this communication we report a new synthesis route for the preparation of alkylcyclophosphazenes of structure IV.



IV

This discovery is of general interest for the following reasons.

(1) Severe limits exist to the types of alkyl groups that can be attached to a phosphazene skeleton via normal Grignard or organolithium reaction techniques. Skeletal cleavage processes complicate these reactions. By contrast, the new synthesis route allows a wide variety of gem-dialkylcyclophosphazenes to be prepared (see the Table) in high yield, and without appreciable skeletal cleavage.

(2) The metallophosphazene reactive intermediate (II) is unique in phosphazene chemistry in its ability to undergo nucleophilic attack on an alkyl halide. In this respect, it opens up new possibilities for the exploration of a wide range of related reactions.

(3) The reaction of II with 1-bromo-2-butene or propargyl bromide illustrates that the phosphazenyl copper intermediate functions as a type of "organocopper" reagent, a result that is important for the development of other reactive metallophosphazene reagents.

(4) The compounds of structure IV are valuable as polymerization "monomers" to yield unusual poly(organophosphazenes).

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